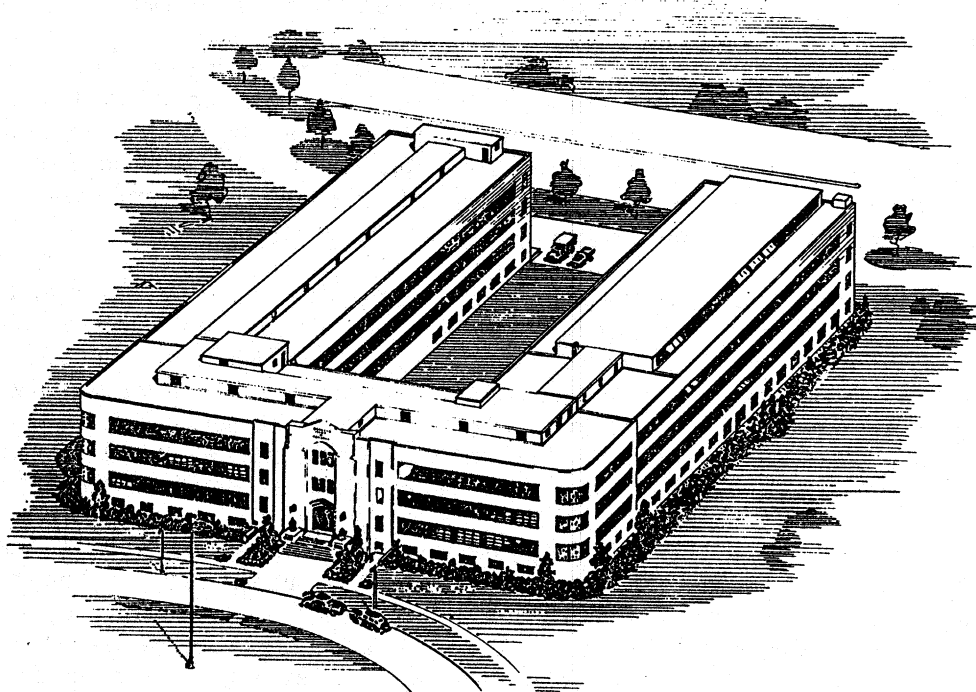


UNITED STATES DEPARTMENT OF AGRICULTURE
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ALLYL STARCH ESTERS

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Allyl starch containing approximately 1.8 to 1.9 allyl groups per glucose unit produces films that, when cured, have high resistance to organic solvents but much less resistance to aqueous solutions such as dilute sodium hydroxide and dilute ethanol. Allyl starch has been found valuable for printing inks, paper coatings, and other applications, but for some uses greater resistance to aqueous solutions is required. One method of improving the resistance might be etherification or esterification of the remaining hydroxyl groups. A previous paper¹ described the preparation and testing of the mixed ethers formed by the reaction of the free hydroxyl groups with alkylating reagents. In the work reported here, allyl starch esters were prepared by the reaction of the free hydroxyl groups with acylating reagents.

Preparation and Testing of Films

In most cases, solutions of the ether-esters of starch used contained 40 to 45 percent solids. Toluene, or toluene containing 5 to 10 percent butanol, was used as solvent. The viscosities of the solutions were usually between 0.5 and 1.0 stokes. Two exceptions were batch 2 (Tables 2 and 3), which had 39 percent solids and a viscosity of 6.27 stokes, and batch 17, which had 35 percent solids and a viscosity of 2.25 stokes.

To determine the time required to cure the films at 100 and 150° C., they were poured on glass plates and heated in an oven for different periods. The time required for cure was based on the results of three tests. If a spot of malachite green could be washed off or if running the edge of a knife along the film (edge knife test) or attempting to lift the film from the glass with the edge of a knife (flat knife test) caused the film to flake off rather than come off in curled strips, a cure was indicated.

Films were cast on test tubes by dipping and cured at 100 and 150° C. The tubes were then suspended in the testing reagents. Some films were protected at their edges and at the bottom of the test tube by a coat of paraffin. This was not done in all cases because the value of such protection was not known until after the work was under way. A more detailed description of the method of preparing and testing the films has been published.¹

For comparison, Table 1 lists some tests on allyl starch itself. The allyl starch esters are listed in Tables 2 and 3. Unless otherwise indicated, the time given in the tables is the time at which the film failed. Zero time indicates failure in less than 3 minutes. When the results were too indefinite or the observations too few to show a more definite time of failure, a range is given. The films were considered to have failed if they were broken at any point or swollen, wrinkled, or blistered over a large area.

¹ E. A. TALLEY, J. H. SCHWARTZ, A. S. HUNTER, AND C. A. BROWN, BENZYL ALLYL STARCH AND OTHER MIXED ALLYL STARCH ETHERS. U. S. DEPT. AGR., BUR. AGR. AND IND. CHEM. AIC-261 (EASTERN REGIONAL RESEARCH LABORATORY), 18 PP. FEB. 1950. (PROCESSED.)

Discussion of Results

Of the films cured at 150° C., films of allyl starch stearate and allyl starch phenyl carbamate showed the greatest general improvement over allyl starch films in resistance to aqueous reagents. The phenyl carbamate, however, was much less resistant to acetone. One batch of allyl starch acetate (No. 2) had much greater resistance to alkaline reagents than did the other. The explanation for this is not clear. It might be due to the fact that this batch (No. 2) was prepared with pyridine as a catalyst, whereas sulfuric acid was used as the catalyst for the other acetate batch (No. 3). Also, the high viscosity of batch 2 (6.27 stokes) might have produced thicker dip-coated films than were obtained from batch 3. Both batches had reduced resistance to acetone. In general, most of the ether-esters showed greater resistance to dilute ethanol and to boiling water than did allyl starch but little or no improvement in resistance to dilute phenol. Some of the ether-esters were not so resistant to acetone as was allyl starch.

Films of allyl starch stearate, oleate, and phenyl carbamate were not cured at 100° C. because of the exceedingly long time required. The allyl starch benzoate could not be tested because its films cracked when dried. Of those films cured at 100° C., only the laurate showed a general improvement over allyl starch. When exposed to some of the reagents, however, its films whitened. One batch of propionate (No. 7) had increased resistance to alkaline reagents. All the ester films cured at 100° C., except those of the allyl starch allyl carbonate, had poor resistance to acetone.

Films of allyl starch and allyl starch esters had greater resistance to acetone as the degree of cure was increased. In the case of the ether-esters, this was true only of films cured at 150° C. The resistance of the ether-esters to dilute phenol also increased with the degree of cure. In many cases, however, films that were undercured (according to the spot and knife tests) showed greater resistance to dilute ammonia solutions than did cured or overcured films.

Allyl starch, allyl starch propionate, linoleate, and allyl carbonate were generally more resistant to the various reagents when cured at 150° C. than at 100°. The improvement produced by the higher temperature was noted mainly in resistance to dilute phenol and ethanol and to acetone. The greater resistance of films cured at the higher temperature had been observed previously with allyl starch, benzyl allyl starch, and other allyl starch mixed ethers.

Allyl starch acetate, propionate, and allyl carbonate took about as long to cure as allyl starch, but the phenyl carbamate and esters of the long-chain fatty acids, except for the linoleate, took much longer. The long curing time may have been due, at least in part, to the free fatty acids. Free linoleic acid did not delay curing because it has drying properties.

Preparation and Analysis of Allyl Starch Esters

Table 4 gives a summary of the preparation of the allyl starch esters. All were prepared from water-free solutions of allyl starch. In most cases,

Table 1. Resistance of allyl starch films to various reagents

Batch No.	Substitution, allyl groups per glucose unit	Curing time	Contact time before failure, hours ¹					
			10% ammonium hydroxide	5% sodium hydroxide	5% phenol	50% ethanol	4% acetic acid	Acetone
		Hours						1% soap solution
20	1.78	2	0	0	0.2	0.3	8-20	1
		2 ₃ p	0.3	0.1	0.7	3.2	72 g	2.3-72
		3	0.7	0.8	0.5	1.1	72 g	3
		4.5	0	0.1	0.2	2	0.4	72 g
		4.5 p	0.2	0.1	2.6	2-6	2	72 g
		6	0.1	0.9	10-19	9.8	10-19	72 g
21	1.57	6 p	0.2	0.5	3.3	1.5	2.7	72 g
		1 p	0.3	0	0	1	72 g	2
		2.5 p ³	0.3	0	0.3	0.4	7	23
		4 p	0.1	0	0.8	5	6.5	72 g
		2 p ₃	0	0	0.2	0.2	2.8	15
		4 p	0	0	0.3	2.8	2.8	72
22	2.1	6 p	0	0	0.4	10	10	72
			0	0				
			0	0				
			0	0				
			0	0				
			0	0				
20 ⁴	1.78	Minutes						
		10	0.4	2	2.1	2.1	72 g	6
		20 ³	2.3	17-20	8-17	3	114 g	8
		50	0.3	0.4	12-22	12-22	72 g	72 g
		100	0.3	0.1	10	25	72 g	72 g
21	1.57	10 p ₃	0.5	0.3	0.6	4.3	27	60
		20 p	0.3	0.3	1	0.8	72 g	72 g
		60 p	0.4	0.3	2	1.3	5.5	72 g
22	2.1	5 p ₃	0.4	0	0.2	3.8	3-8	2.5
		10 p ₃	0	0	0.7	23	28	72 g
		40 p	0	0	0.4	0.6	0.6	72 g

1 g indicates that the film was not attacked; w indicates that the film wrinkled but became smooth and adhered to the glass on removal from the reagent.

2 p indicates that the film was protected.

3 Proper cure, as indicated by spot and knife tests.

4 In boiling water, the films failed in 0.1 to 0.2 hour.

Table 2. Resistance of films of allyl starch esters to various reagents (films cured at 150° C.)

Batch No.	Substituent (R)	Substitution, groups per glucose unit		Curing time, mins. ²	Contact time before failure, hours ¹							Boiling water	1% soap solution
					10% ammonium hydroxide	5% sodium hydroxide	5% phenol	50% ethanol	4% acetic acid	Acetone			
2	Acetyl	1.15	1.76	0.09	20	72	0.5	0.7	114 g	0.4			114 g
3 ³	Acetyl	1.23 ⁴	1.73	0.04	20	0.4	0.3	72 g	72 w	1		72 g	72 g
					40 ⁵	0.3	0.3	72 g	72 w	3	6	57	45
6	Propionyl	1.21	1.73	0.06 ⁴	70	0.2	0.5	72 g	72 g	20	1.8		
					20 ⁵	24	0.4	21	74 g	0.1	9 g	96	96
8 ³	Propionyl	1.24 ⁴	1.73	0.03	60	0.3	1.5	96 g	96 g	1	6	96	96
					70	0.2	1.5	4	96 g	0.4; 0.4 ⁶	6	96	96
7 ⁷	Propionyl	1.34 ⁴	1.60	0.06	20 p ⁵	0.1	0.3	72 g	72 g	3.5	10 g	72	72
					40 p ⁵	0.1	0.8	72 g	72 g	8		36	36
9	Lauroyl	1.24	1.8	0.0	70 p	0.1	3.4	72 g	72 g	72 g		10	10
					80 p	0.1							
10 ³	Lauroyl	0.7	1.84	0.5	20 p ⁵	72 g	0.1	0	72 g	0		72 g	72 g
					40 p ⁵	15	0.2	0.1	72 g	3		72 g	72 g
11	Stearoyl	0.5	2.14	0.4	120	1.5	0.5	96 g	96 g	52	2.7	72 g	72 g
					180 ⁵	0.5							
12	Oleyl	1.2	1.84	0.0	240	0.7	1	72 g	72 g	72 g		72 g	72 g
					960 ⁸	0.3	5.6	72 g	72 g	72 g	5	72 g	72 w
13	Linoleyl	0.9	2.04	0.1	1320	0.5	15	72 g	72 g	72 g	6 g	72 g	72 g
					1740	0.5		72 g	72 g	72 g	7	60	60
15	Allyl carbonyl	0.37	1.89 ⁴	0.74	210 ⁹	0.5	4.5	72 g	72 g	72 g		72 g	72 g
					960 ⁸	0.8	3.5-19	72 g	72 g	72 g		72 g	72 g
17	Phenyl carbamyl	0.50	2.06	0.44	1320	1.5	3.5-19	72 g	72 g	72 g		72 g	72 g
					1740	0.3	0	3-19	3-19	57 g		3-19	3-19
12	Oleyl	1.2	1.84	0.0	20 p ⁵	0.3	0	75 w	82-75	0.9		75 w	75 w
					30 p ⁵	0.8 ¹⁰	0.1	75 w	82-75	0.7		75 w	75 w
13	Linoleyl	0.9	2.04	0.1	40 p	0.9 ¹⁰	0.1	75 w	75 w	75 w		75 w	75 w
					195 ⁵	0.1	4	2.2	45	72 w		72 w	72 w
15	Allyl carbonyl	0.37	1.89 ⁴	0.74	20	0.1	4	72 g	72 g	0.1; 0.1 ⁶	6.2 g		
					50	72 w	0.6	72 g	72 g	1.5			
17	Phenyl carbamyl	0.50	2.06	0.44	195 ⁵	72 w	1.6	72 g	72 g				
					195 ⁵	72 w							

1 g indicates that the film was not attacked; w indicates that the film wrinkled but became smooth and adhered to the glass on removal from the reagent.

2 p indicates that the film was protected.

3 Prepared from allyl starch batch 20.

4 By difference.

5 Proper cure, as indicated by spot and knife tests.

6 Check sample.

7 Prepared from allyl starch batch 21.

8 Not cured in 1260 minutes; cure time not known.

9 Cure indicated by edge knife test and rubbing with toluene-moistened paper but not by the other tests. Film resisted toluene for 0.4 hour.

10 Film darkened upon exposure to reagent.

Table 3. Resistance of films of allyl starch esters to various reagents (films cured at 100° C.)

Batch No.	Substituent (R)	Substitution, groups per glucose unit R Allyl Hydroxyl	Curing time, hours, 2	Contact time before failure, hours ¹							Boiling water	1% soap solution	
				10% ammonium hydroxide	5% sodium hydroxide	5% phenol	50% ethanol	4% acetic acid	Acetone				
2	Acetyl	1.15	1.76	0.09	5	0.5	0.5	1.8	1.9	98 w	0.3	98 c	
3 ³	Acetyl	1.23 ⁴	1.73	0.04	1 p ⁵	3	4-19	0	72 w	72 w	0	1	
					3 p ⁵	1.2	0.6	0	40	72 w	0	3	
					6 p	0.3	0.2	0	32-52	72 w	0.1	6 g	
6	Propionyl	1.21	1.73	0.06 ⁴	2.5	0.3	1.9	0.5	5-21	117 w	0.1	4	
					3 ⁵	0.4	0.3	0.5	5-21	117 w	0.3		
					4.5	0.2	0.5	1	30	117 w	3		
8 ³	Propionyl	1.24 ⁴	1.73	0.03	2 p ⁵	1.6	0.7	0.1	72 g	72 w	0.1	72 w	
					4 p ⁵	0.5	0.1	0.3	72 g	72 w	0.6		1.8
					6 p	0.2	0	0.3	72 w	72 w	0.2		
7 ⁷	Propionyl	1.34 ⁴	1.60	0.06	3 p ⁵	74 w	10	0	0	72 q	0	72 c	
					6 p ⁵	36	6	0	72	72 q	0		72 c
					8 p	36	5.5	0	72	72 g	0		
10 ³	Lauroyl	0.7	1.8 ⁴	0.5	1 ⁹	90 w	90	3-18 ⁸	90 ⁸	90	0.1	90 w	
					3 ⁹	90 ⁸	90	3-18 ⁸	90 ⁸	90	0		1 ⁸
					6	90 w ⁸	90	20 ⁸	90 ⁸	90	0		
13 ¹⁰	Linoleyl	0.9	2.0 ⁴	0.1	16	30	72 g	21 ⁸	24 ⁸	72 g	0	72 c	
					3 ⁵	5.2	0.1	0	22	75 g	0.1		28-3
					4 ⁵	5.2	0.1	0	0.1	75 g	0.1		
15	Allyl Carbonyl	0.37	1.89 ⁴	0.74	5	0.6	0.1	0	0.6	75 g	0.1	28-5	
					3	0	0	1.9	1.9	1.9	98 w		0.1

¹ g indicates that the film was not attacked; w indicates that the film wrinkled but became smooth and adhered to the glass on removal from the reagent.

² p indicates that the film was protected.

³ Prepared from allyl starch batch 20.

⁴ By difference.

⁵ Proper cure, as indicated by spot and knife tests.

⁶ Check sample.

⁷ Prepared from allyl starch batch 21.

⁸ Whittened on exposure to reagent.

⁹ Not cured in 3 hours; time required for cure unknown.

¹⁰ Films only slightly attacked by toluene in 75 hours.

Table 4. Preparation of allyl starch esters

Batch No.	Acylation reagent	Excess, %	Catalyst, moles per mole acylation reagent ¹	Solvent added	Reaction time, hours	Temp., °C.	Acyl groups per allyl	Substitution, per glucose unit, allyl hydroxy ¹	Yield, %
1	Acetic anhydride	100	Pyridine, 1.5	Benzene	0.7	80	0.73	0.41 ²	78
	"	100	"	"	1.3	80	0.78	0.35 ²	
	"	100	"	"	2.3	80	0.94	0.22 ²	
	"	100	"	"	4	80	1.12	0.04 ²	
2	"	100	Pyridine, 1	Toluene	5.8	90	1.15	0.09	77
3	"	100	H ₂ SO ₄	"	15	90	1.23 ²	0.04	
4	Propionic anhydride	100	Pyridine, 1.5	Benzene	0.5	80	0.58	0.58 ²	
	"	100	"	"	1.0	80	0.68	0.47 ²	
	"	100	"	"	2.1	80	0.74	0.40 ²	
	"	100	"	"	4.0	80	0.77	0.37 ²	
	"	100	"	"	7.9	80	0.89	0.25 ²	
5	"	100	Pyridine, 1.28	Benzene	6	95	1.14	0.06 ²	> 91
	"	100	"	"	10.5	95	1.18	0.02 ²	> 91
	"	100	"	"	12.8	95	1.22	0	> 91
6	"	100	Pyridine, 1	Benzene	13.1	85	1.21	0.06 ²	
7	"	100	Pyridine, 1	"	13.5	80	1.34 ²	0.06	88
8	"	100	H ₂ SO ₄	Toluene	15	90	1.24 ²	0.03	70
9	Lauryl chloride	50	Pyridine, slightly over 1	8 Toluene: 1 Benzene ³	8	80	1.2	0.0	
10	Lauric acid	0	Ca + Ba acetates	Xylene	14.4	153-217	0.7	0.5	67
11	Stearic acid	0	Ca + Ba acetates	Toluene ⁴	5.6	140-240	0.55	0.45	
12 ⁶	Oleic chloride	87	Pyridine, 1.18	Toluene	10	80	1.2	0.0	96
13 ⁶	Linoleic chloride	97	Pyridine, 1.1	Toluene	8	80	0.9	0.1	100
14	Allyl chlorocarbonate	100	Pyridine, 1	8 Toluene: 1 Benzene ³	3	80	0.44	0.70	
	"	100	"	"	6	80	0.46	0.70	
15	Benzoyl chloride	100	Pyridine, 1	8 Toluene: 1 Benzene ³	6.2	80	0.37	0.74 ²	68
16	Phenyl isocyanate	0	Pyridine, 1.6	Benzene	14.2	85	1.20	0.12 ²	> 82
17	"	0	"	Toluene	3	128	0.50	0.44	
18	"	0	"	"	13.6	80	0.96	0.18	
19	"	0	"	Toluene	13.7	80	0.89	0.22	100

Where pyridine is listed, it served also as a solvent.

¹ By difference.² Parts by weight.³ A few milliliters of xylene was added toward end of reaction.⁴ Approximate analyses.⁵ Prepared from allyl starch supplied by General Mills, Inc.⁶

benzene or toluene was used as the solvent, but in some of the batches that used pyridine as an acid-binding agent and solvent, only a small amount of the water-immiscible solvent was used to remove the water by entrainment before the acylating reagent was added. In general, 1 to 3 parts by weight of solvent (including pyridine but not the acylating agent) to one of allyl starch was used. Batches 18 and 19, however, were prepared with 3.5 and 4 parts of solvent, respectively. Most of the reactions were carried out in a 1-liter three-necked flask fitted with an addition tube, reflux condenser, calcium chloride tube, and Hershberg stirrer (no stirring in batches 1 and 4).

Allyl starch acetate and propionate were prepared by adding acetic or propionic anhydride to an allyl starch solution containing either a pyridine or sulfuric acid catalyst and heating in a bath at 80 to 90° C. (95° for batch 5). The amount of sulfuric acid used was equal to 0.38 percent of the amount of allyl starch (by weight); the amounts of pyridine used are listed in Table 4. The esters were purified by precipitating them in water, first from the reaction mixture, then from acetone solution. If too much benzene or toluene was present, the reaction mixture was first neutralized and steam-distilled. The gum was then dissolved in acetone and precipitated.

Allyl starch laurate, oleate, linoleate, and allyl carbonate were prepared from the corresponding acid chlorides. The flask was placed in an ice bath, and the acid chloride was added dropwise (with stirring) over a half-hour period. The ice bath was then removed, and the flask was heated to 80° C. For the oleate and linoleate, a nitrogen atmosphere was maintained during heating. In one batch of allyl carbonate (No. 15), the acid chloride was added dropwise but in three portions; the second and third portions were added after the batch had reached reaction temperature. The laurate, oleate, and linoleate were purified by adding ether to precipitate the pyridine-acid chloride complexes, filtering, and washing in a separatory funnel with sodium carbonate or bicarbonate followed by distilled water. Washing was difficult because of formation of emulsions, and considerable amounts of free acid remained. The allyl carbonates were purified by steam distilling (in batch 15 the complexes were first precipitated with ether), dissolving in acetone, and precipitating in water.

The preparation of the benzoate was similar to that of the other esters for which acid chlorides were used as acylating reagents, but the benzoyl chloride was added at room temperature, and a reaction temperature of 85° C. was used. The ester was obtained by neutralizing and steam distilling the reaction mixture. The gum was then dissolved in toluene and washed with water containing a little ammonia (pH 8 or 9).

Allyl starch stearate and one batch of laurate (No. 10) were prepared by reaction with equivalent amounts of stearic and lauric acids, respectively. A mixture of three parts of calcium acetate monohydrate to one part of barium acetate monohydrate was used as catalyst.² The weight of catalyst

² J. D. BRANDNER, R. H. HUNTER, M. D. BREWSTER, AND R. E. BONNER, DRYING OILS FROM SORBITOL AND LINSEED FATTY ACIDS, IND. ENG. CHEM., 37, 809-12 (1945).

equaled 0.5 percent of the weight of allyl starch plus fatty acid. A thermometer was immersed in the mixture, the mixture was heated to reflux, and the water of esterification was removed continuously by entrainment with toluene or xylene. During the reaction, the temperature was raised by distilling off part of the solvent. The highest temperature reached for the laurate was 217° C.; the highest for the stearate was 240°. Both esters were purified by heating with calcium hydroxide, removing the water formed by distilling at reduced pressure, and filtering out the calcium soaps. Direct esterification produced only partial substitution; attempts to obtain complete substitution by this method caused gelation.

Phenyl isocyanate was used to make the allyl starch phenyl carbamates³. In two of the batches (Nos. 18 and 19), pyridine was used as a catalyst. The mixtures were heated with stirring, batch 17 at 128° C., and batches 18 and 19 at 80° C. Batch 17 was purified by steam distilling and precipitating in water from acetone solution. Batches 17 and 18 were treated with ethanol to remove any remaining isocyanate, after which batch 18 was precipitated in 37 percent ethanol (by weight), filtered, and steam-distilled.

Except for the linoleyl chloride, the acylating reagents were all commercial products. The linoleyl chloride (containing 87 percent linoleyl chloride and 13 percent oleyl chloride) was prepared from a mixture of cottonseed oil acids purified by the method of Frankel and Brown.⁴

The esters were mostly light-tan gums, brittle at room temperature. The esters of the long-chain fatty acids, however, were soft to almost liquid; their films tended to be dark. All the esters were soluble in toluene. In batches 2 and 15, a little butanol was needed to clarify the solutions. The long-chain fatty acid esters were insoluble in acetone or at least in moist acetone. All the other esters dissolved in acetone.

In most cases, a high degree of substitution was obtained. The substitution was lower in the allyl starch allyl carbonates, the laurate and stearate prepared by direct esterification, and the phenyl carbamate prepared without a catalyst.

The esters were analyzed by determining any two of the three functional groups--allyl, acyl, or hydroxyl--and subtracting from three (the maximum possible substitution) to get the substitution of the third group. Esters that were soft at room temperature were left in solution for analysis; the other analytical samples were prepared as described by Hamilton and Yanovsky⁵. Allyl groups were determined by the Wijs method⁵. The method of hydroxyl determination was a modification¹ of the method of Malm, Genung, and Williams⁶. Acyl groups were determined by the alcoholic alkali method

³ A SIMILAR REACTION WAS CARRIED OUT BY I. A. WOLFF AND C. E. RIST, POLYSACCHARIDE ARYL CARBAMATES, J. AM. CHEM. SOC., 70, 2779-82 (1948).

⁴ J. FRANKEL AND J. B. BROWN, THE ISOLATION OF PURE LINOLEIC ACID BY CRYSTALLIZATION, J. AM. CHEM. SOC., 63, 1483-4 (1941).

⁵ R. M. HAMILTON AND E. YANOVSKY, MIXED ALLYL ETHERS OF STARCH, IND. ENG. CHEM., 38, 864-6 (1946).

⁶ C. J. MALM, L. B. GENUNG, AND R. F. WILLIAMS, JR., ANALYSIS OF CELLULOSE DERIVATIVES, DETERMINATION OF FREE HYDROXYL CONTENT, IND. ENG. CHEM., ANAL. ED., 14, 935-40 (1942).

of Genung and Mallatt⁷. Free acidity was determined by dissolving the samples in 95 percent alcohol and titrating with one-tenth normal sodium hydroxide. For the phenyl carbamates, Kjeldahl nitrogen determinations were also made⁸. Wijs determinations gave too high results for the phenyl carbamates, possibly because of a reaction between the Wijs solution and the phenyl carbamyl group.

Summary and Conclusions

Allyl starch acetate, propionate, laurate, stearate, oleate, linoleate, allyl carbonate, benzoate, and phenyl carbamate were prepared. Films of these esters (except the benzoate) were compared with allyl starch films for resistance to 10 percent ammonia, 5 percent sodium hydroxide, 5 percent phenol, 50 percent ethanol, 4 percent acetic acid, and undiluted acetone. Some tests were made also with 1 percent soap solution and boiling distilled water.

The esters in general showed greater improvement over allyl starch in resistance to aqueous reagents than did the allyl starch mixed ethers¹. But in most cases, the resistance of the esters to acetone was low, and the esters that showed the greatest over-all resistance, namely, the laurate, stearate, and phenyl carbamate, had a long curing time. They therefore would not be suitable for applications in which the film should harden quickly. The long curing time required for the laurate and stearate may be due in part to free acid.

In comparing the allyl starch esters with the allyl starch mixed ethers, it should also be noted that the allyl starch mixed ethers can be prepared by a one-step process, but because of the necessity of removing water before the acylating reagent is added, the allyl starch esters must be made by a two-step process.

The tests were all made on unmodified films. Better resistance might be shown by properly plasticized films cured to the optimum degree of cure for the use for which they are intended.

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⁷ L. B. GENUNG AND R. C. MALLATT, ANALYSIS OF CELLULOSE DERIVATIVES, IND. ENG. CHEM. ANAL. ED., 13, 372 (1941); SEE ALSO I. A. WOLFF, D. W. OLDS, AND G. E. HILBERT, THE ACYLATION OF CORN STARCH AMYLOSE AND AMYLOPECTIN, J. AM. CHEM. SOC., 73, 347 (1951).

⁸ KJELDAHL DETERMINATIONS WERE MADE BY L. R. ROSS AND C. RICCIUTI OF THIS LABORATORY.